U.S. EPA Analytical Methods for the Analysis of Perchlorate in Drinking Water

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Early IC Methods

- **Concern over perchlorate in the early 90's prompted development of early Ion Chromatography (IC) methods**
- **California Dept. of Health Services, June 1997**
  - IC Method with Suppressed Conductivity Detection
  - AS5 analytical column, required eluent modifier (p-cyanophenol)
  - Method was approved for CA State monitoring
  - High Total Dissolved Solids (TDSs) can impact analysis

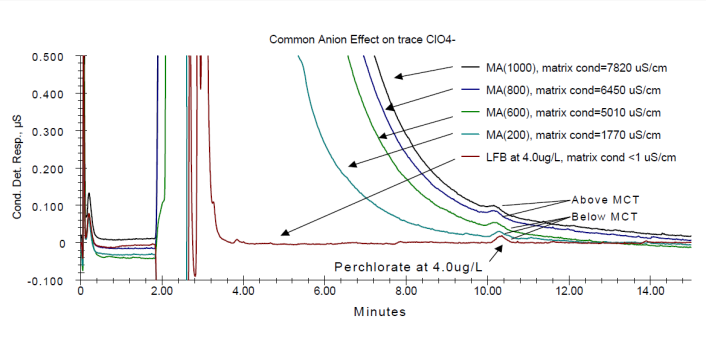
Early IC Methods

- **New column technologies eliminated need for eluent modifier**
- **Dionex Corporation, 1998, Application Note 121**
  - IC Method with Suppressed Conductivity Detection
  - AS11 analytical column, no eluent modifier needed
  - Adopted as approved alternate for CA State monitoring
  - High TDSs are less of an impact but still can affect analysis

Development of EPA 314.0

- **Further advances in analytical column technology**
- **Interest in establishing a standard EPA test method**
- **EPA Method 314.0, revision 1.0, November 1999**
  - IC Method with suppressed conductivity detection
  - Minimum Reporting Level (MRL) of 4.0 ug/L with detection limit (DL) of 0.5 ug/L
  - High capacity AS16 analytical column, no eluent modifier
  - AS16 further reduces TDS effect
  - Includes additional safeguard to monitor and reduce TDS
  - Sample matrix spike evaluation for confirmation
  - Widely adopted as the standard perchlorate method

Superimposed IC Chromatograms Indicating the Influence of High Concentrations of Common Anions on Low Concentration Measurement of Perchlorate at 4.0 ug/L



Additional Method Development Goals

- **Reduce MRL to < 1ug/L through application of:**
  - Sample concentration techniques
  - Microbore analytical columns
  - Advanced detection systems, i.e., mass spectrometry (MS)
- **Further increase tolerance for high ionic strength matrices**
- **Enhance measurement selectivity**

Method 314.1, revision 1.0
May 2005

- **Lowered the MRL to < 0.2 ug/L (DL 0.03 ug/L) using online sample pre-concentration**
- **Uses matrix diversion to handle high ionic strength matrices (up to 1000 mg/L TDS)**
- **Added confirmation analysis using a second analytical column**

Method 314.2, version 1.0
May 2008

- **Lowered the MRL to < 0.1 ug/L (DL 0.02 ug/L) using large volume injection**
- **Uses 2-D chromatography to handle high ionic strength matrices (up to 1000 mg/L TDS)**
- **2-D chromatography eliminates the need for separate confirmation analysis**

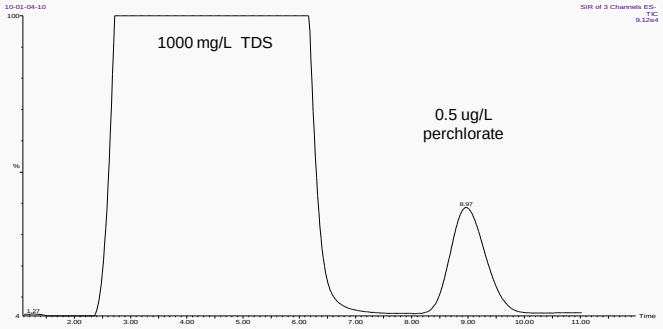
Method 331.0, revision 1.0
January 2005

- **Lowered the MRL to < 0.1 ug/L (DL < 0.01 ug/L)**
- **Applied multiple analytical advancements to an LC analysis**
  - A perchlorate selective LC column (AS-21)
  - MS or MS/MS detection for selectivity and sensitivity
  - A custom labeled internal standard ($Cl^{18}O_4$)

Method 332.0, revision 1.0
March 2005

- **Lowered the MRL to 0.1 ug/L (DL 0.02 ug/L)**
- **Applied multiple analytical advancements in an IC analysis**
  - Suppressed conductivity IC
  - MS or MS/MS selectivity and sensitivity
  - A custom labeled internal standard ($Cl^{18}O_4$)

331.0 MS/MS Chromatogram with high TDS



Method	Expected Reporting Limit (ug/L)	MDL (ug/L)	Cycle Time Minutes	Acceptable Performance in 1000mg/L TDS	Confirmation	Complexity	Relative Cost
314.0	4.0	0.53	11	No	Matrix Spike Assessment	Moderate	$45 - $85
314.1	0.14	0.03	25 (50 with confirmation)	Yes	Second Column Analysis	High	$60 - $110
314.2	0.06	0.018	37	Yes	2-D	High	$60 - $110
331.0	0.022 (MS/MS) 0.056 (SIM)	0.005 (MS/MS) 0.008 (SIM)	9	Yes	MS/MS or MS	Moderate	$80 - $180
332.0	0.10 (SIM)	0.02 (SIM)	8	Yes	MS	Moderate	$80 - $180